NOVEL PHOTOCATALYSTS AND PROCESSES FOR THE DESTRUCTION OF CHEMICAL WARFARE AGENTS (CWA)

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ABSTRACT

The present research project aims at developing novel photocatalysts for the destruction of chemical warfare agents to innocuous products in gas and liquid phases. The project focuses on understanding the chemistry involved during photodegradation of selected simulants, which can effectively represent chemical warfare agents such as HD, G-type (GA, GB, GD) and VX. Studies addressing the destruction of toxic organics found in other military activities (solvents, purification centers, etc.) will be performed as well. The project combines the synthesis and characterization of novel catalysts, catalytic evaluations with probe molecules and kinetic studies to understand the lability of certain bonds (C-S, C-P, P=O, etc..). Moreover, the project focuses on the development of effective slurry and gas phase reactors including "closed cycle" systems, photocatalysts, which operate with visible/solar radiation and finally use of novel processes such as ultrasound to enhance the photochemical transformation and avoid formation of any toxic intermediates.

This paper describes the initial work and research tasks undertaken for testing selected categories of photocatalysts for destruction of organics and CWA simulants, utilization of ultrasound for enhancement of reactant transformation and elimination of byproducts, and development of photocatalysts for operation with visible light. More specifically, we present the initial work we performed on the photodegradation of diethylsulfide (DES) in gas phase (C_2H_5-S-C_2H_5) as a simulant of mustard gas (HD) over various titanias utilizing UV light. The main routes of DES degradation are C-S cleavage, S oxidation, α-C and β-C oxidation were revealed. The liquid phase photodegradation of organics in the presence of ultrasound aiming at the enhancement of catalyst reactivity and elimination of any byproducts was studied as well. Effective photocatalysts for operation with visible light were synthesized based on transition metal substituted and loaded MCM-41. Extensive work is being performed involving the use of the above approaches for CWA simulants such as diethylsulfide, 2-chloro ethyl-ethyl-sulfide ($Cl(CH_2)_2SCH_2CH_3$) and dimethyl-methyl-phosphonate (DMMP).

INTRODUCTION

Over the last decade, numerous studies have been performed aiming at the development of novel technologies for the successful and economic destruction of CWAs to benign products. In view of the seriousness of the problem, the National Research Council (NRC) recommended a new research program [1] to address the chemical neutralization and biodegradation of CWAs. Since then, several attempts combining different methods have been performed. The existing state-of-the-art on this subject has been reviewed in detail by Yang and coworkers [2, 3].

The present research project is a multiyear effort and aims at developing novel photocatalysts, reactors and processes for the destruction of chemical warfare agents to innocuous products in gas and liquid phases. The project focuses on understanding the chemistry involved during photodegradation of selected probe molecules which can effectively represent chemical warfare agents such as HD, G-type (GA, GB, GD) and VX. The project combines the synthesis and characterization of novel catalysts, catalytic evaluations with probe molecules and kinetic studies to understand the lability of certain bonds (C-S, C-P, P=O, etc..). Moreover, the project focuses on the development of highly

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effective slurry and gas phase reactors including "closed cycle" systems, photocatalysts, which operate with visible/solar radiation and finally use of novel processes such as ultrasound to enhance the photochemical transformation and avoid formation of any toxic intermediates. This paper describes the initial work and research tasks undertaken for testing selected categories of photocatalysts for destruction of CWA simulants, utilization of ultrasound for enhancement of reactant transformation and elimination of byproducts, and development of photocatalysts for operation with visible light.
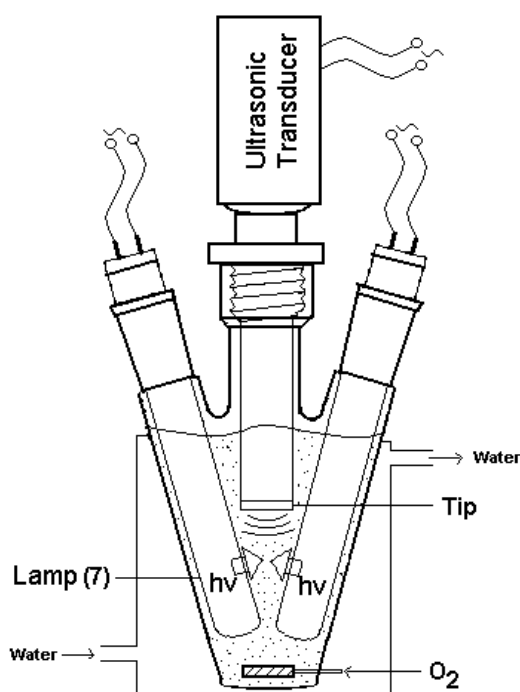
EXPERIMENTAL

Figure 1. Sonophotocatalytic reactor for the degradation of organics.

Preliminary photocatalytic experiments were performed using four different samples of titanium dioxide: Hombikat UV 100 (Sachtleben Chemie GmbH), Degussa P25 with 50 m^2/g, Degussa P25 with 75 m^2/g, and homemade TiO_2. Diethyl sulfide (Fluka) as a simulant of HD and deionized water were used. Photocatalytic degradation of diethyl sulfide over a thin film of photocatalysts was accomplished in a flow reactor. The set up used in this study has been described in detail in our earlier work [4]. The reactor was a stainless steel cylindrical vessel illuminated through a Pyrex window placed on the top of the reactor. Two types of light sources were employed to illuminate the catalyst: two 4 W fluorescent lamps (Wiko, Japan) and 450 W mercury lamp (Hanovia). This type of experiments constitutes the initiation of research for understanding the kinetic pathways for the destruction of HD simulants in gas and liquid phases. The first results are described in [5]. Additional work involving CWA simulants such as diethyl-sulfide (DES) and dimethyl-methyl –phosphonate (DMMP) in liquid phase is being performed [6].

The photocatalytic activity of the selected titania powders was evaluated using salicylic acid in oxygenated aqueous suspensions in order to test the effect of ultrasound. Salicylic acid (Fisher) and titania used in the study were of reagent grade. Photocatalytic experiments were performed in a custom-made ultrasonic reactor presented in Figure 1, which contained seven pyrex immersion wells hosting the UV lamps. The reactor consisted of a working volume of 1 L and was surrounded by a glass jacket to allow circulation of cooling water to maintain the reaction temperature at 30±2°C. Seven UV-irradiated black light fluorescent lamps (4 W each) with a peak intensity at 375 nm were used and were placed inside the pyrex immersion wells (cutoff wavelength 320 nm). The agitating action of a stirrer and ultrasound assured adequate mixing of the suspension of titania particles inside the reactor. The ultrasonic tip (1x7 cm) delivered 100 W of ultrasound into the reaction space at the frequency of 20 kHz. Pure oxygen gas (Wright Brothers, 99.5%) was sparged through the vessel utilizing a stainless steel bubbler at a rate of 500 cm^3/min. The experiments involving CWA simulants and ultrasound are being performed and very promising results are collected [6].

Transition metal substituted MCM-41 supports with Si/Me=80 and Si/Ti=40 were synthesized using Ludox HS-40 (DuPont) as the source of silica. The precursors used for the incorporation of transition metal oxides in the framework of MCM-41 were vanadia: $VO(C_3H_7O)_3$ (Alfa); chromia: $CrCl_3$ (Fisher); iron (III) oxide: $Fe_2(SO_4)_3$ (Fisher); titania: titanium isopropoxide (Aldrich). All samples were prepared in the presence of hexadecyltrimethylammonium bromide (Fluka) as a template. The final mixtures were stirred together for 30 minutes, then transferred into polypropylene

bottle and treated under autogenous pressure without stirring at 90 - 100°C for 3 days. The resulting solids were filtered, washed, dried, and calcined at 550°C for 10 hours under air flow. The support (typicaly 1.5 g) was dispersed in ~100 ml of isopropanol, and titanium isopropoxide was added to achieve 25 % loading. The system was dried while stirring at ambient temperature. It was then placed in the oven to dry at 100°C for 1 hour and later were calcined at 450°C for 3 hours.

The photocatalytic testing included the degradation of organic compounds, which was performed in a batch round flat-plate reactor using 200 W medium pressure mercury lamp (Ace Glass) as the light source. A 0.25" thick plexiglas filter was utilized for the purpose of excluding ultraviolet radiation when conducting visible-light experiments. Several reactants were tested for the photocatalytic degradation: 2,4,6-trichlorophenol (Fisher), chlorophenol (Aldrich), formic acid (Fisher).

RESULTS AND DISCUSSION

No dark reaction of DES degradation was detected over all catalysts studied at room temperature. The second type of blank experiment was carried out in order to check the possibility of photochemical transformation of diethyl sulfide under the light. No conversion of diethyl sulfide was

$$CH_3CH_2\text{-}S\text{-}CH_2CH_3$$

| C-S cleavage | S oxidation | α-C oxidation | β-C oxidation |

$CH_3CH_2\text{-}SO\text{-}CH_2CH_3$ $CH_3CH_2\text{-}S\text{-}CH_2CH_2OH$

CH_3CH_2OH $CH_3CH_2S^{\cdot}$ $CH_3CH_2\text{-}S\text{-}CO\text{-}CH_3$

C_2H_4 $CH_3CH_2\text{-}SO_2\text{-}CH_2CH_3$

CH_3CHO $(CH_3CH_2)_2S_2$
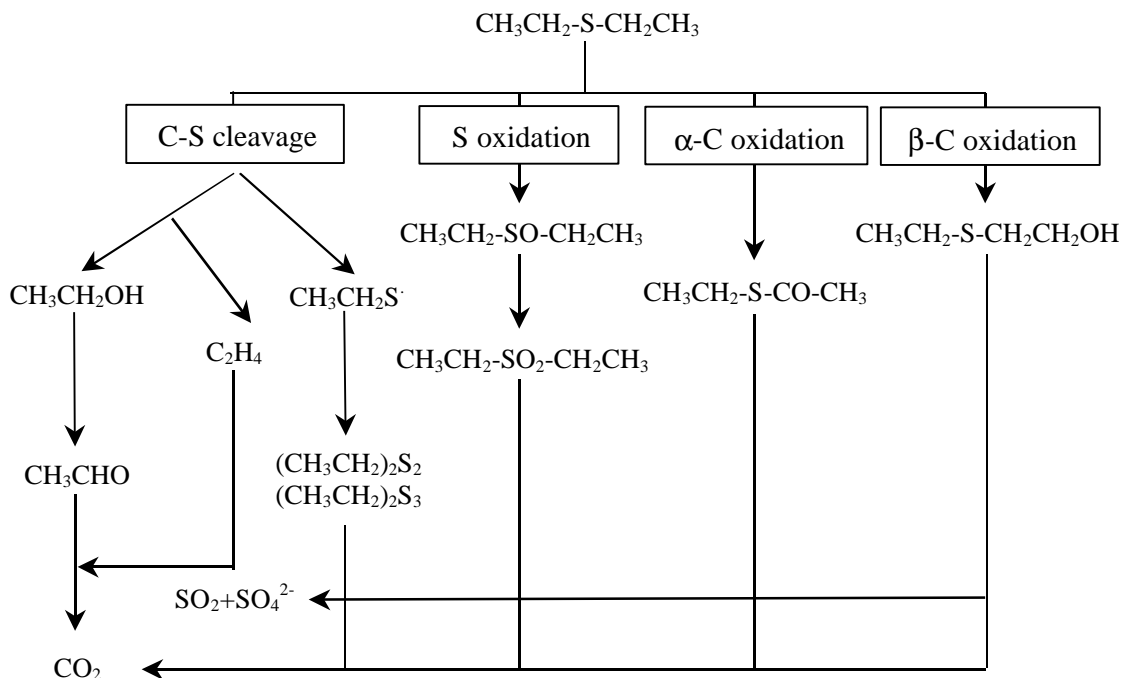$(CH_3CH_2)_2S_3$

$SO_2 + SO_4^{2-}$

CO_2

Figure 2. Reaction scheme of the photocatalytic degradation of diethyl sulfide based on the products detected.

detected during this test at air humidity 25% (21°C). Hence, only heterogeneous photocatalytic processes cause all the transformation of diethyl sulfide over TiO_2 under ultraviolet light in the system applied. Switching on the lamps of the reactor initially led to high initial conversion of diethyl sulfide (up to 90%). Photocatalytic destruction of diethyl sulfide resulted in the formation of the same gaseous products in different proportions over all catalysts tested in the current work. Gaseous products comprised ethylene, carbon dioxide, acetaldehyde, ethanol, sulfur dioxide, S-ethyl ethanethioate, and diethyl disulfide. The extract in isopropanol from the surface of TiO_2 Hombikat UV 100 operated during 23 hours at humidity 19% and temperature 26°C in diethyl sulfide destruction contained the following products: diethyl sulfoxide and smaller quantities of diethyl disulfide, diethyl sulfone, 2-ethylthioethanol, and diethyl trisulfide. Acid products and salts (such as sulfates), which are produced at the final stage of the oxidation of sulfur in diethyl sulfide were not detected because of their extremely low volatility. Only diethyl disulfide was detected in both gaseous and surface products. Other products distributed between gas and surface according to their volatility.

On the basis of the set of detected products it is possible to derive conclusions about the routes of diethyl sulfide destruction (Fig. 2).

Such products as ethanol and ethylene clearly testify to the contribution of C-S bond cleavage (corresponding branches in Fig. 2). The cleavage can be deemed to proceed through hydrolysis to form ethanol and rearrangement to form ethylene. However, the intermediate product of hydrolysis (ethylthiol) was not detected in the products. This may be related to the high lability of this intermediate at the reaction conditions. Dimerization of surface $CH_3CH_2S^\bullet$ species results in diethyl disulfide. Further C-S bond cleavage in this disulfide and interaction of $CH_3CH_2SS^\bullet$ and $CH_3CH_2S^\bullet$ surface species can explain the formation of diethyl trisulfide. It should be noted that although diethyl disulfide was present in the initial diethyl sulfide feed, its concentration in the reactor effluent was well beyond its initial concentration, especially in experiments with high light intensity (as will be shown later in the study).

The second obvious route of diethyl sulfide photocatalytic destruction is the oxidation of sulfur atom. The products of this oxidation pathway (sulfoxide and sulfone) resided on the surface of catalyst, where they could be further oxidized leading to the formation of inorganic compounds. The third route is the oxidation of the α-carbon, which resulted in the formation of low concentrations of CH_3CH_2-S-CO-CH$_3$ in the gas phase. Such route was also present in the photocatalytic degradation of the oxygen analog of diethyl sulfide, diethyl ether, and led to the formation of ethylacetate [7]. The last route of diethyl sulfide photocatalytic oxidation is the oxidation of the β-carbon. Small quantities of $CH_3CH_2SCH_2CH_2OH$ were detected on the surface of catalyst, which signifies the presence of this fourth route of degradation. The proposed above four routes of the photocatalytic destruction of diethyl sulfide represent only initial stages of transformation. During further deeper reaction, these routes can intersect each other. For example, after oxidation of β-carbon the oxidation of sulfur could take place. Finally, the photocatalytic oxidation results in inorganic oxides, H_2O, CO_2, and SO_2.

The phenomena of cavitation *i.e.* the nucleation, growth and collapse of bubbles in a liquid are due to the chemical effects of ultrasound [8, 9, 10]. The collapse of the bubbles induces localized supercritical conditions: high temperature, high pressure, and electrical discharge effects. The consequences of these extreme conditions are the cleavage of dioxygen molecules and water molecules forming $H^\bullet$ and $^\bullet OH$ radicals. From the reactions of these entities ($O^\bullet$, $H^\bullet$, $^\bullet OH$) with each other and with H_2O and $^\bullet O_2^-$, $HO_2^\bullet$ radicals and H_2O_2 are formed. Therefore, the combination of photocatalytic and ultrasonic irradiation can enhance the degradation of organic pollutants in water by the species, notably $^\bullet OH$ radicals.

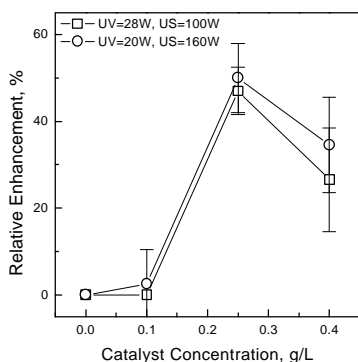$$\overset{))))}{H_2O \rightarrow H^\bullet + {}^\bullet OH} \tag{1}$$

Figure 3. Enhancement by ultrasound for Hombikat UV 100.

The photodegradation of salicylic acid was employed to test the simultaneous effect of photodestruction and sonication [11]. Salicylic acid was the probe molecule we used originally, but currently we are studying selected CW simulants [6]. With salicylic acid we found that ultrasound augments the chemical transformation. More specifically, we found that the use of ultrasound eliminates the organic byproducts, something which is unique for the effective destruction of organics since organic byproducts resulting during the photodegradation can be equally toxic with the reactants themselves.

Now let us study the effect of the catalyst mass by comparing the behavior of HK at 0.1, 0.25, and 0.4 g/L concentration. As expected, the conversion after 3 hours is the greatest for the larger concentration of the catalyst and the smallest for the smallest concentration of the catalyst. For some systems (as described in [14]) the reaction rate decreases with the increase in the catalyst concentration after a certain threshold value. However, we observed that this threshold value of

catalyst concentration has not been achieved for the system HK/salicylic acid, since the rate increases monotonically in the sequence 0.1, 0.25, and 0.4 g/L of titania with and without the ultrasound. Moreover, comparing the enhancement of the reaction rate (defined as the absolute difference between the two reaction rates divided by the rate of photocatalysis alone) imparted by the presence of ultrasound reveals a different trend (Figure 3).

The enhancement is negligible for the low concentration of the catalyst (see Figure 2a). This is due to the insufficient number of centers of bubble disruption in the solution since the presence of solids significantly enhances this process [12]. As a result, the ultrasound passes through the slurry without imparting energy into it and with little formation of active radicals. On the other hand, relatively low concentrations of solids usually correspond to smaller aggregate sizes [13], which are more difficult to break in order to expose more surface area to the light. The enhancement of the activity is the largest for the intermediate concentrations of titania (0.25 g/L) as shown in Figure 3. This is a combined effect of the full attenuation of light [14], aggregate breakage by ultrasound due to the action of its shear stress, and generation of radicals by the ultrasound itself upon impingement onto solid particles. The low value of enhancement by ultrasound for higher concentrated suspensions can be explained by the fact that the working volume of the slurry becomes low [15]. Indeed, from the high values of the extinction coefficients one cannot expect the light to penetrate far into such an optically dense medium. As a result, there is no enhancement due to aggregate breakage, as the zone of action of light is far away from the zone of action of ultrasound. Therefore, one has to use higher ultrasound power and less attenuating powders to achieve adequate enhancement of photocatalytic activity in highly concentrated suspensions.

Photocatalysts for the operation in visible light (potential utilization of solar radiation) are employed. We have initiated an effort in this direction and our original results utilizing simple organic probe molecules are very promising [16]. Our catalysts are based on a methodology we developed to synthesize transition metal incorporated MCM-41 molecular sieves loaded with titania. Ongoing research in our labs focuses on testing the most effective photocatalysts for the destruction of CWA simulants utiliziang visible light. The time course of the photodegradation of formic acid on visible-light irradiated catalysts is shown in Figure 4.
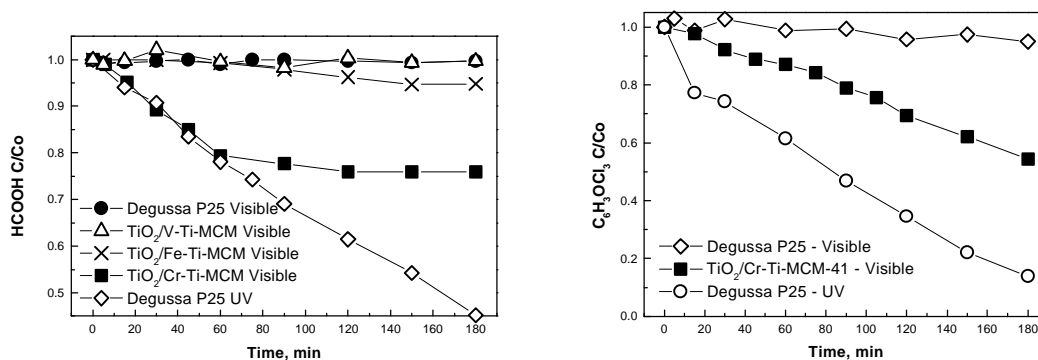

Figure 4. Time course of the photodegradation of formic acid (left) and 2,4,6-trichlorophenol (right) in visible light on transition metal substituted titania loaded MCM-41 materials.

Non-reduced (as calcined) chromium substituted MCM-41 with loaded titania did exhibit activity comparable with that of Degussa P25 in UV (Fig. 4). For the TiO_2/Cr-Ti-MCM-41 the concentration of formic acid decreases steadily for about 60 min, then levels off at approximately 25 % of conversion. This behavior is unexpected, since from a physics point of view the altervalent cations (especially with the oxidation state of +5) would serve best as dopants [17], but we will see later that the primary doping species in the above catalysts is Cr^{+6}. Iron substituted MCM-41 sieves loaded with titania also exhibit some photoactivity (Fig. 4). The concentration of formic acid monotonically decreases and levels off at about 6 % of conversion, which was proved in three independent experiments. The maximum degradation rate is considerably lower than that of neat titania (P25) in UV. Such behavior can be explained on the basis of the structure of neat Fe-Ti-MCM-41. The activity

of TiO₂/V-Ti-MCM-41 was also explored under identical operation conditions (Fig. 4). However, no discernible conversion of formic acid under visible light was detected.

The performance of the most active catalyst (TiO₂/Cr-Ti-MCM-41) was also tested for the photodegradation of phenolic compounds in visible light. As seen from Fig. 4, the above specimen exhibits photoactivity to decompose 2,4,6-trichlorophenol. This is also the case for 4-chlorophenol (not shown). The activity for the degradation of these reactants in visible light is not as high as that of Degussa P25 in UV. As in the case of Degussa P25, the activity acquires lower values with the smaller number of chlorine atoms in the reactant molecule, primarily due to the lesser generation of secondary active chlorine radicals [18]. No deactivation is observed for the above two reactions in visible light, contrary to the photodegradation of formic acid. Apparently, the chlorine atoms help to re-activate the catalyst.

In order to explain the general trend in the activity of the catalysts employed in visible light, one may note that the lowest activity (close to zero) was exhibited by the V-Ti-MCM-41 based powder. It should be noted that the oxidation state of five is the most stable for vanadium at ambient conditions. Furthermore, its transformation into other oxidation states in aqueous solution is very unlikely. This is the primary reason for low activity. This is because no effect of doping took place. Indeed, considering the absorption spectrum of V-doped catalysts (not shown) reveals that they lack shoulders corresponding to dopant levels. As a result, the sublevel allowing for double photon excitation is not observed. Such double step excitation would promote the electron to the conduction band of titania by the absorption of two low-energy quanta in visible range. On the contrary, the most active catalysts (TiO₂/Cr-Ti-MCM-41 and to a much lesser extent TiO₂/Fe-Ti-MCM-41) have two stable oxidation states (Cr^{+3} and Cr^{+6}, Fe^{+2} and Fe^{+3}) both of which are found inside and outside the framework of MCM-41, which was also shown by our own XPS results. Only ions that are in the framework can act as dopants for titania, as they are atomically dispersed, unlike bulk oxides outside the framework. Furthermore, in our materials we have two types of heterojunctions: framework ions (V, Cr, or Fe)–titania and extra-framework metal oxide-titania. The first type allows to excite the photocatalyst by absorbing two photons in the visible part of the spectrum (reaction 2). The second type can consume the trapped electrons produced by the doped titania, wherein the dopant is represented by the transition metal ions in the framework (reaction 3). Finally, the free hole reacts with the aqueous medium to form active radicals (reaction 4):

$$MeTiO_x \rightarrow h^+ + e^- \text{ (trapped)} \qquad (2)$$
$$e^- \text{(trapped)} + MeO_x \rightarrow MeO_{x-0.5} \qquad (3)$$
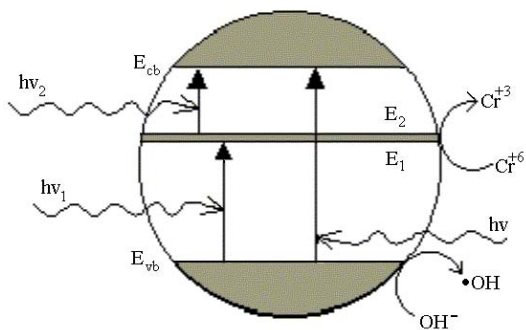$$h^+ + OH^- \rightarrow \bullet OH \qquad (4)$$

Figure 5. Mechanism of the photodegradation on transition metal substituted MCM-41.

where Me is the transition metal employed. The trapping of electrons and holes by the dopant was detected in doped titania [19]. This phenomenon is deleterious for the photocatalytic activity. However, we propose that the presence of a reducible oxide (for example, CrO_3) in close proximity allows to scavenge the trapped electrons (as shown in Fig. 5). For the case of chromium substituted MCM-41, such oxide was detected by our own XPS studies. As the result, the extra-framework transition metal oxide attains the lower oxidations state (for example, extra-framework CrO_3 becomes Cr_2O_3). At the same time, the valence band holes of titania become available to oxidize water and produce hydroxyl radicals (reaction 4), which constitute the major oxidant in aqueous heterogeneous photocatalysis. The maximum activity obeys the following pattern: Cr > Fe >> V. This clearly corresponds to the difference in the number of electrons between the two stable oxidation states of each transition metal. It is three for chromium and one for iron.

CONCLUSIONS

The distribution of diethylsulfide products strongly suggests that the two main pathways of the degradation are the oxidation of sulfur and carbon atoms and hydrolysis of the C-S bond. The products of the complete oxidation (SO_2 and CO_2) were detected in very small quantities, most of the products correspond to C-S bond cleavage and partial oxidation. Further efforts should be devoted to make photocatalytic oxidation suitable for the complete mineralization of reduced sulfur compounds. Other CWA simulants are being tested by using simultaneously photocatalysis and somication aiming at rapid destruction of the reqctants and complete elimination of organic byproducts.

Several transition metal based titania loaded MCM-41 (Si/Me=80, titania content – 25 wt%) materials were tested for the degradation of organics in visible light. The chromium substituted MCM-41 was found to serve as the best support for titania to achieve the highest degradation rates of formic acid, 2,4,6-trichlorophenol, and 4-chlorophenol. The change in the state of the catalyst during the reaction was observed for Cr substituted molecular sieves, which led to its deactivation. XPS revealed increased surface concentrations of Cr ions upon the loading of TiO_2, which at the same time allows to minimize the leaching of chromium ions. The mechanism of the photodegradation in visible light on titania loaded transition metal substituted MCM-41 is proposed. It consists of double step excitation by visible light, as opposed to conventional single step excitation by UV light

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